Separation and Capture of CO_2 Using a High Temperature Pressure Swing Adsorption (PSA) System

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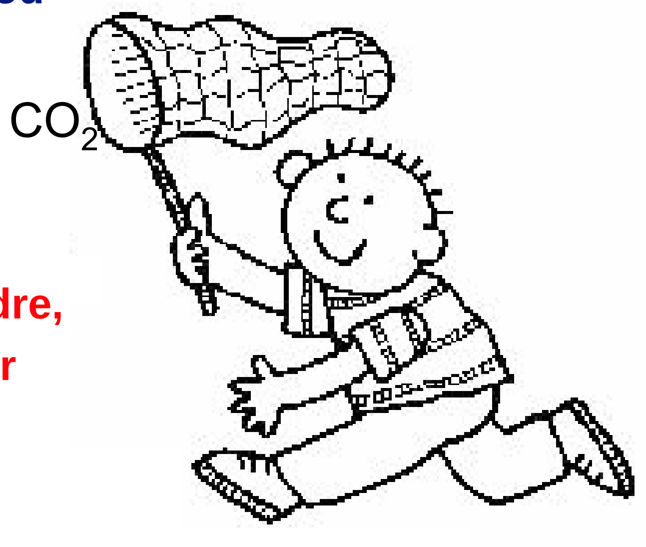


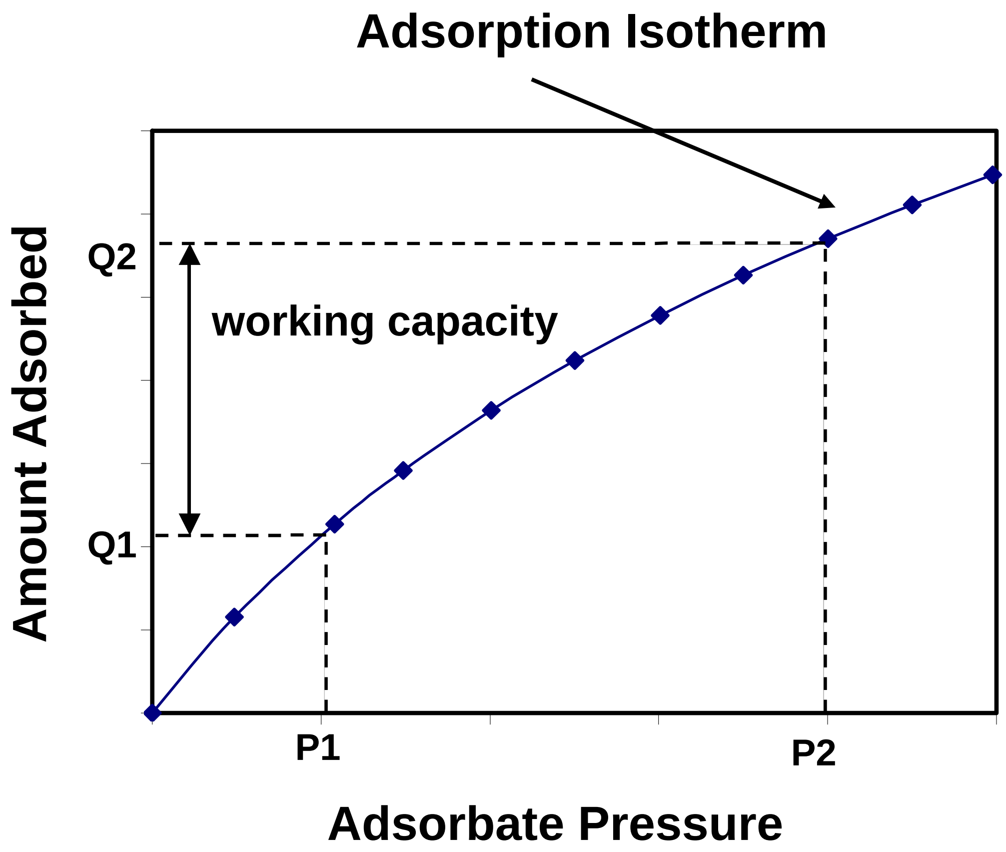
Third Annual Conference on Carbon Capture and Sequestration
May 3 - 6, 2004
Alexandria, Virginia

USC - EPA Collaboration

- University of South Carolina
  - "Radically New Adsorption Cycles for Carbon Dioxide Sequestration" (DOE/NETL)
  - Development and modeling of new Pressure Swing Adsorption (PSA) cycles
    - Traditional Stripping Reflux (SR)
    - Enriching Reflux (ER) and Dual Reflux (DR)

- US EPA Office of Research and Development
  - Sorbent development, characterization, and optimization
  - Relate structure and chemical nature of the sorbents to the adsorption properties

Pressure Swing Adsorption (PSA)



Used industrially for many gas separations

Vacuum Swing Adsorption (VSA) and Temperature Swing Adsorption (TSA) are variants

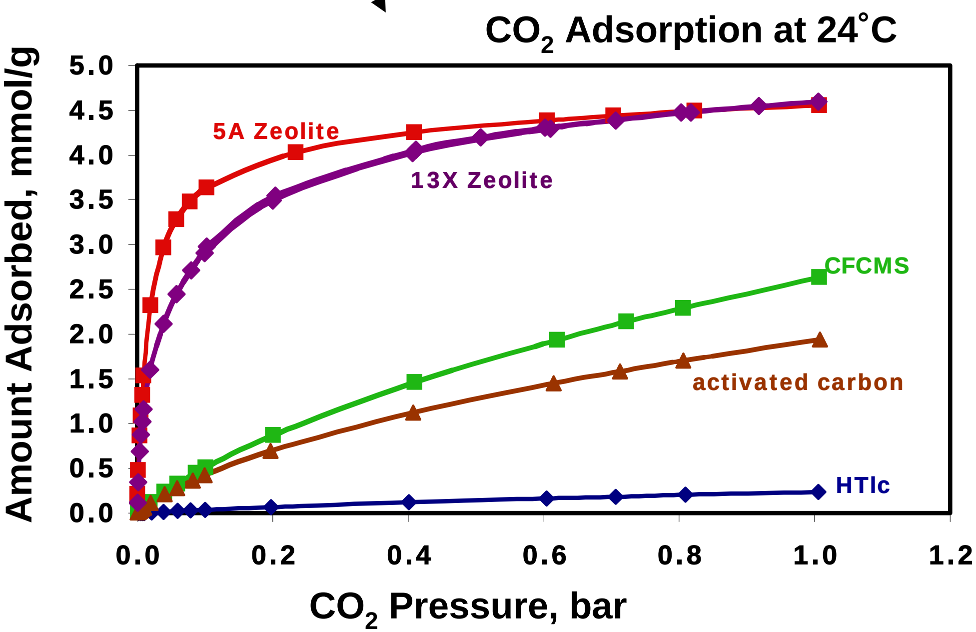
PSA has been proposed for CO_2 separation and capture

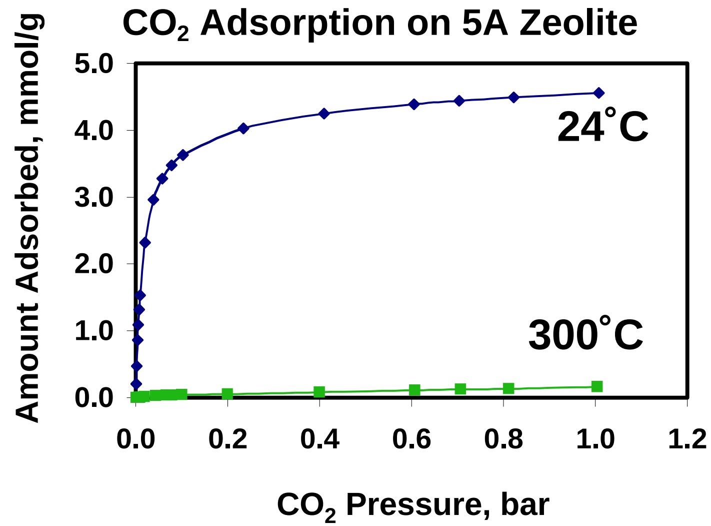
Pressure Swing Adsorption (PSA)

- The viability of PSA for gas separations is dependent on:
  - The PSA cycle operating conditions
    - Purge-to-feed ratio
    - Pressure ratio (P_H/P_L)
    - Cycle times, etc.
  - The effectiveness of the sorbent
    - Capacity (working capacity)
    - Stability (hydrothermal/mechanical and cycling)
    - Kinetics

Adsorption of CO_2 on Solid Sorbents

There are many commonly used sorbents (*e.g.*, zeolites, activated carbon, carbon MS) that have good CO_2 capacity at room temperature



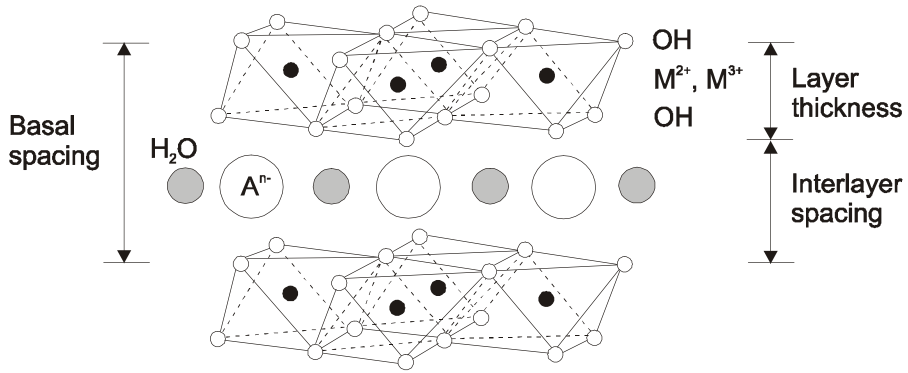


However, the capacity is greatly diminished at elevated temperatures - and in the presence of steam

Hydrotalcite-like Compound (HTlc)

Also known as Layered Double Hydroxides (LDHs)

Anionic clays (bi-dimensional basic solids)



$[Mg_{0.73}Al_{0.27}(OH)_2](CO_3)_{0.135}\bullet mH_2O$

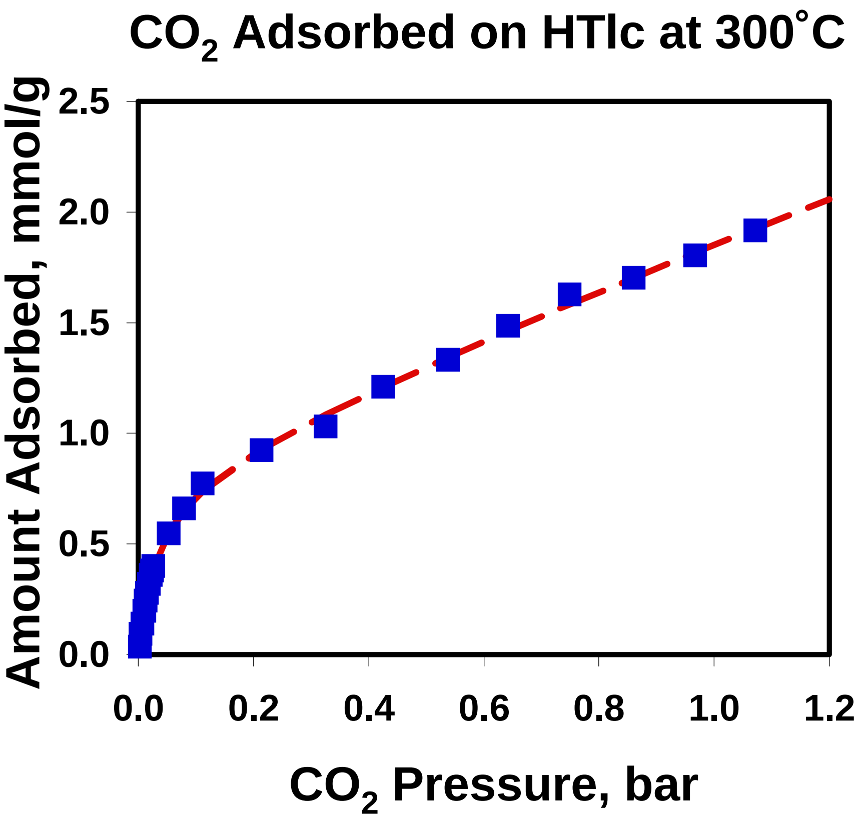
$\left.\begin{array}{l}\text{Layer thickness} \approx 4.8\ \text{Å} \\ \text{Interlayer spacing} \approx 3.0\ \text{Å} \\ \text{Basal spacing} \approx 7.8\ \text{Å}\end{array}\right\}$ unheated

Have been used as

- catalysts and catalyst supports
- adsorbents and ion exchangers for treatment of liquid wastes,
- in medicine (as antacids).

The structure consists of positively-charged layers with interlayer space containing charge compensating anions and water molecules

Adsorption of CO_2 on HTlc



$$Q = \underbrace{\frac{q_{mp} b_p P}{1 + b_p P}}_{\text{physisorption}} + \underbrace{\frac{q_{mc}}{2s} \ln\left[\frac{1 + b_c P e^{s}}{1 + b_c P e^{-s}}\right]}_{\text{chemisorption}}$$

q_{mp} = 0.7890 mmol/g

b_p = 30.99 bar^{-1}

s = 1.923

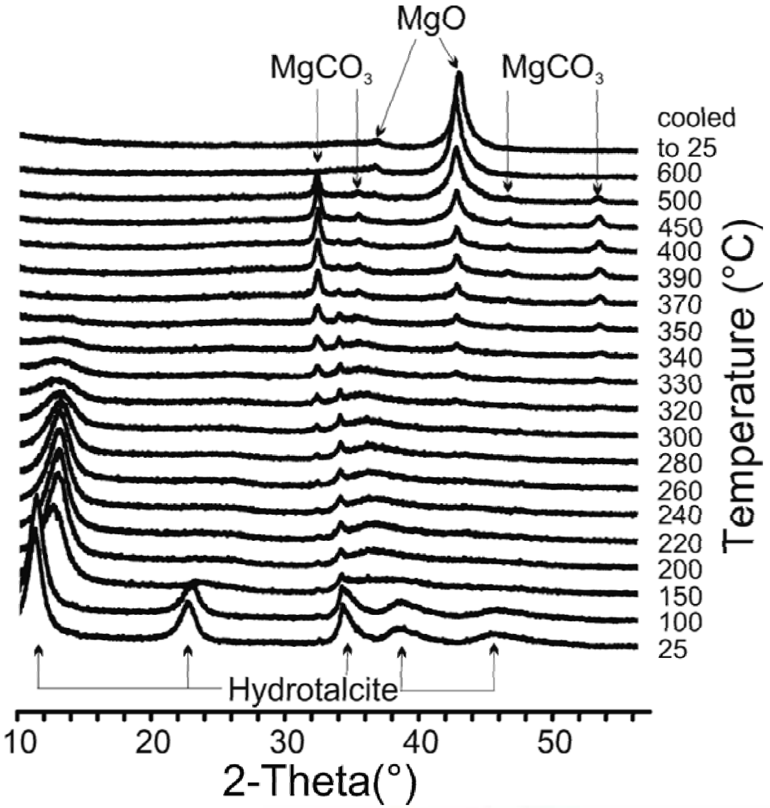
q_{mc} = 40.17 mmol/g

b_c = 0.0164 bar^{-1}

Sorbent Characterization

We have done considerable characterization of the various HTlc sorbents (including high temperature XRD at ORNL)

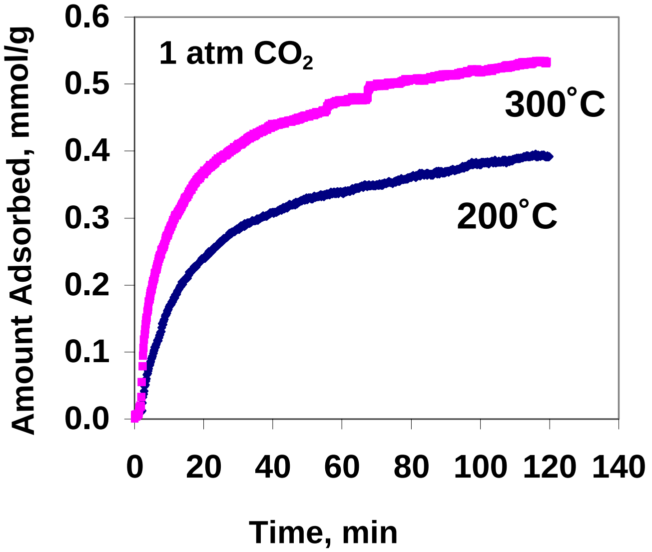
This has given us insight into the role of structure and chemical properties (*e.g.*, surface basicity) on the adsorption of CO_2 at high temps.

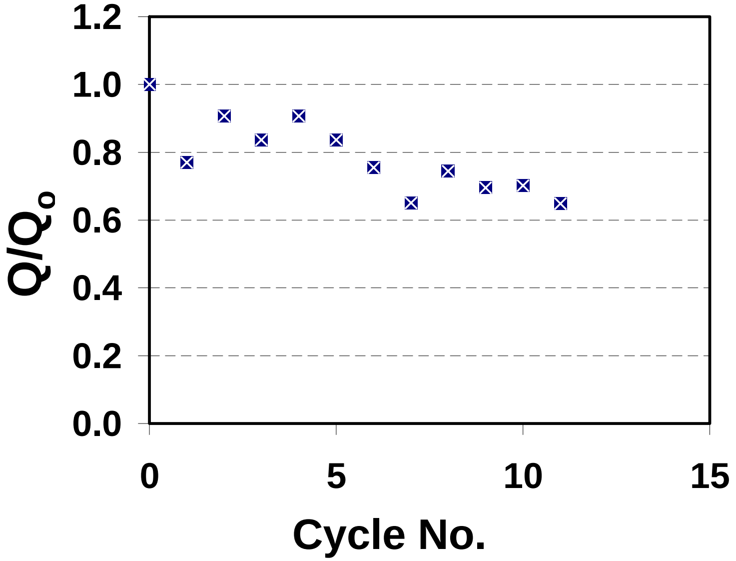


OAK RIDGE NATIONAL LABORATORY

Sorbent Development

- HTlcs have very good CO_2 capacity and selectivity at high temperature
- Slow kinetics
- Some loss of capacity with adsorb/desorb cycling





PSA Development at University of South Carolina

At USC, traditional (referred to as stripping reflux, SR) as well as **new PSA technologies** are being explored for separation of CO_2 from flue gas streams at elevated temperatures.

- These new technologies are referred to as **enriching reflux (ER)** and **dual reflux (DR)** PSA cycles, which are in stark contrast to the **conventional stripping reflux (SR)** PSA cycles.

- In contrast to traditional PSA separation processes, these new PSA cycles have been specially designed for **enriching the heavy component**, in this case carbon dioxide.

- New HTlcs being developed by the EPA are being provided to USC for analysis and evaluation using in-house developed SR, ER and DR rigorous PSA process simulators.

Cyclic Adsorption Process Simulator Development at USC

- rigorous simulators of stripping, enriching and dual reflux (SR, ER and DR) pressure swing adsorption (PSA) cycles being developed for design, optimization and understanding

- ideal, equilibrium theory based simulators of SR, ER and DR PSA being developed for best possible performance and understanding

- approximate SR PSA calculators for education, training and in some cases feasibility

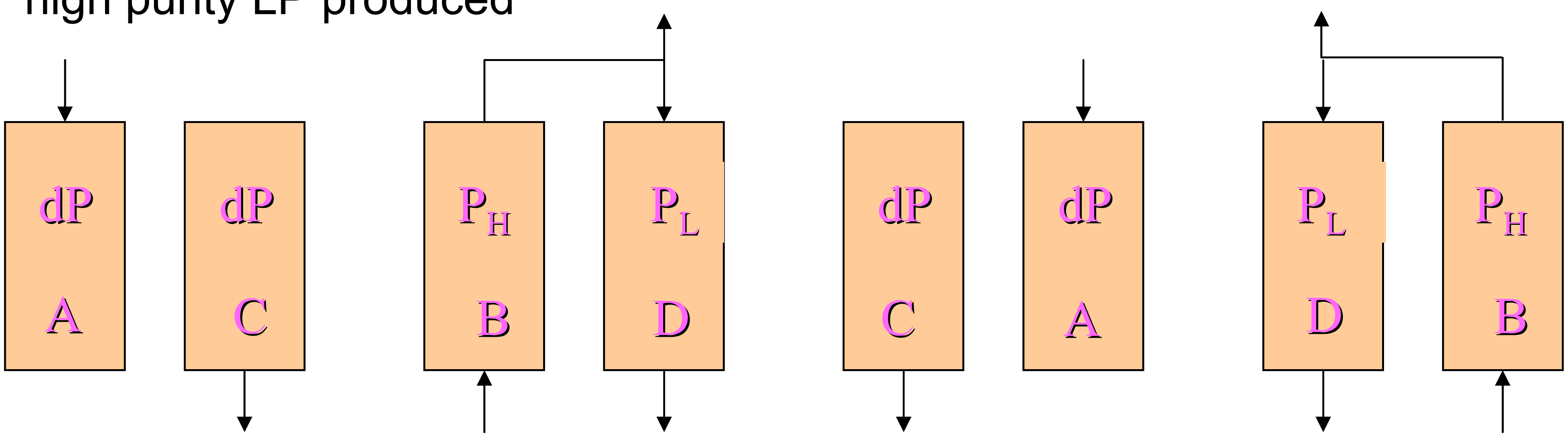
- SR PSA LabView based simulator with control room type visualization for education and training

Cyclic Adsorption Process Objectives

- describe **stripping reflux (SR) PSA** process that can be used for CO_2 concentration and recovery at high temperature
- introduce SR-PSA model assumptions
- discuss hydrotalcite adsorbent and process and operating conditions
- present initial simulation results for a twin bed, 4-step SR PSA cycle designed to concentrate CO_2 from a stack gas at high temperature using a hydrotalcite adsorbent
- show methodology to determine **optimum operating conditions** for a **real system** (i.e., for a non isothermal-mass transfer limited system)

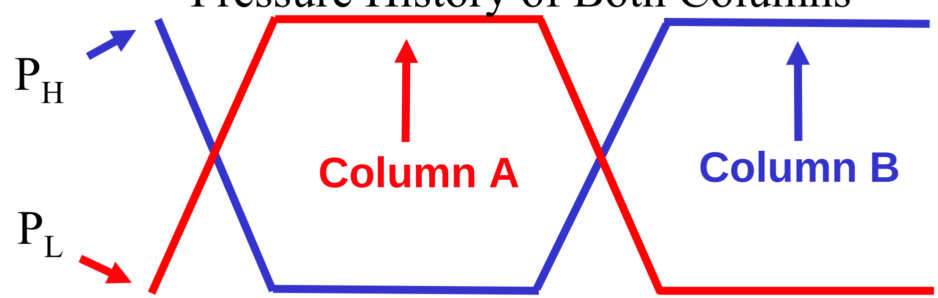
Stripping Reflux (SR) PSA Cycle

- typical 4-step Skarstrom type SR PSA cycle utilized
- countercurrent (CC) blowdown and light product (LP) pressurization utilized
- many other SR PSA cycle configurations exist and being explored
- high purity LP produced



A: light product (LP) pressurization
B: high pressure feed
C: countercurrent (CC) blowdown
D: countercurrent low pressure purge

Pressure History of Both Columns



SR-PSA Model Assumptions

ASSUMPTIONS:

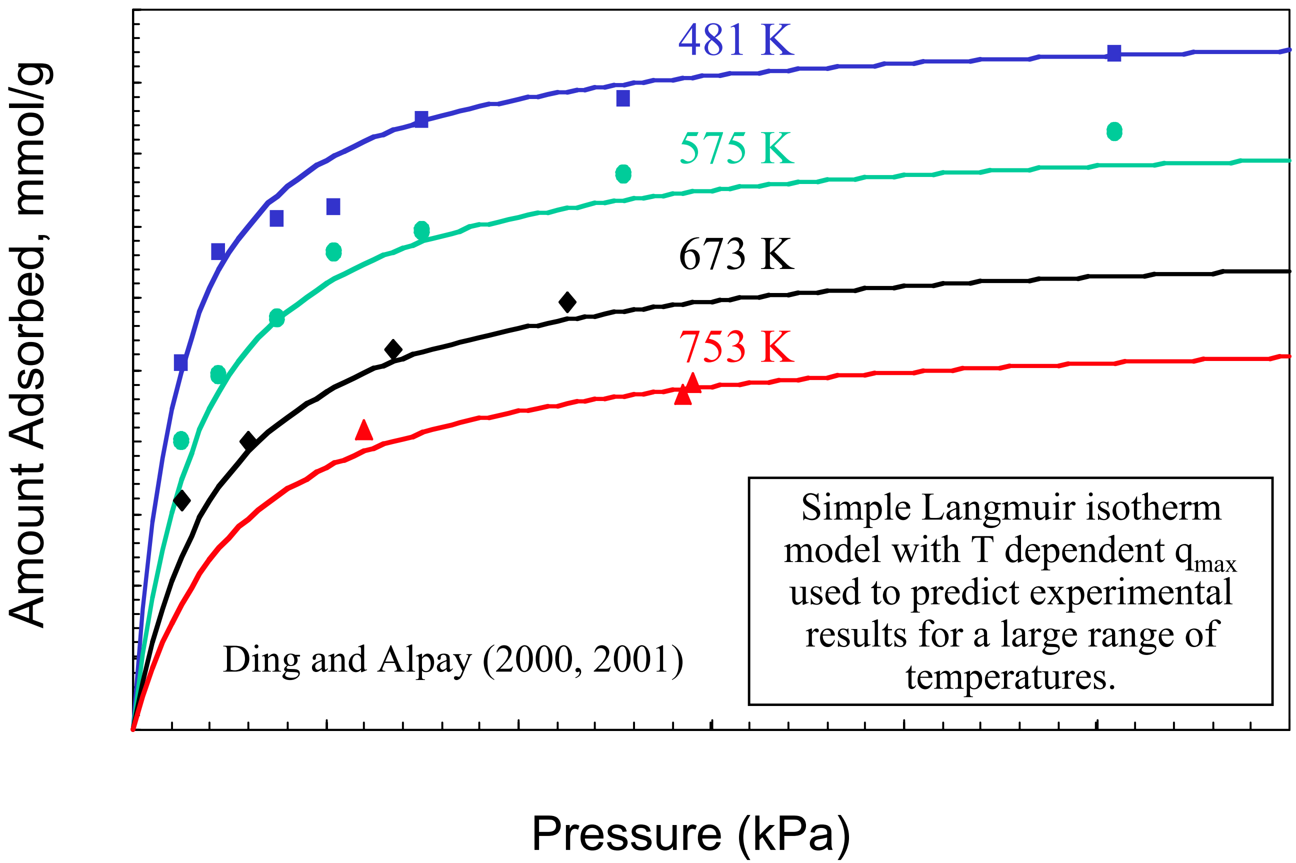
- ideal gas law
- plug-flow (negligible radial gradients)
- negligible pressure drop
- finite heat and mass transfer resistances
- mass transfer governed by linear driving force approximation
- heat transfer governed by overall heat transfer coefficient
- loading dependent heat of adsorption
- gas and adsorbed phase heat capacities equal and temperature dependent
- constant adsorbent heat capacity

SOLUTION PROCEDURE:

- optimum conditions found through extensive parametric studies
- FORTRAN based numerical code (method of lines) uses (DDASPK)

NON-ISOTHERMAL, MASS TRANSFER LIMITED MODEL!

CO_2 Adsorption Isotherms on Hydrotalcite



Literature values were used as an initial start to evaluate the SR PSA model

Bed Characteristics, Adsorbent Properties, and Transport Properties for SR-PSA Model

Bed Dimensions and Operating Conditions	L_b (m)	2.724×10^{-1}
	r_b (m)	3.87×10^{-2}
	Q_F (SLPM)	2.0
	T_F, T_o (K)	575
Adsorbent Properties	ε_b	0.48
	ρ_p (kg/m^3)	1563
	r_p (m)	1.375×10^{-3}
	$C_{p,s}$ (kJ/kg/K)	0.850
Heat and Mass Transfer Coefficients	h_b (kW/m^2/K)	0.00067
	$k_{CO2,ad}$ (s^{-1})	0.0058
	$k_{CO2,de}$ (s^{-1})	0.0006

Different Mass Transfer Rate Constants for Adsorption and Desorption

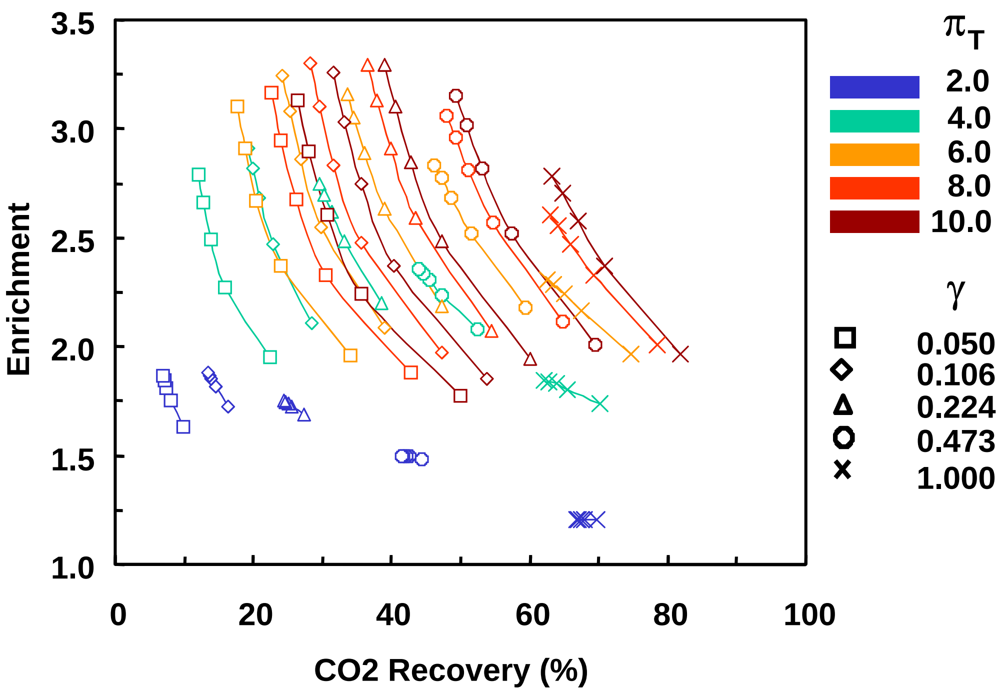
Ding and Alpay (2000, 2001)

Operating Parameters Investigated with SR PSA Model

Cycle Time	$t_{Bl/Pr}$ (s)	60
	$t_{F/P}$ (s)	100, 200, 300, 400, 500
	t_c (s)	320, 520, 720, 920, 1120
Feed Concentration	$y_{F,CO2}$	0.15
	$y_{F,N2}$	0.75
	$y_{F,H2O}$	0.10
Pressure Ratio	P_H/P_L	2.0, 4.0, 6.0, 8.0, 10.0
	P_L (kPa)	2.76×10^1 (4 Psia)
Purge to Feed Ratios	γ	0.050, 0.106, 0.224, 0.473, 1.000

Preliminary Results from SR PSA Model

Conditions: $y_{A,F} = 0.15$, $P_L = 4$ psia



- Each line represents runs for fixed π_T and γ and varying $t_{F/P}$
- Conditions for optimal SR-PSA operation clearly observed:
  - Curves closer to upper right corner of plot more appropriate
- Enrichments of 3.0 to 3.5 easily obtained with up to 60% CO_2 recovery despite restricting mass transfer limitation-**very encouraging results so far!**
- Larger γ are still required, while π_T seems close to optimum
- Up to this point, compromise between recoveries and enrichments still unavoidable:
  - Other elements (e.g., cost) required to determine optimum $t_{F/P}$

Conclusions

- Hydrotalcite-like compounds (HTlcs) show great promise as high temperature CO_2 solids sorbents.

- Adsorption and desorption kinetics must be improved.

- Simple 4-step SR PSA cycle is able to produce enriched CO_2 with moderate recovery in a high temperature process; 5-step cycle probably better.

- SR-PSA model providing considerable insight into which parameters appear to be most important to maximizing both the enrichments and recoveries.

Path Forward

- The HTlcs are very open to structural and chemical manipulation.
- Considerable insight has already been gained into the relationship between structure and chemical composition and the adsorption characteristics. This work will continue.
- Much more research being done to determine the optimum operating conditions not only for SR, but also for ER and DR PSA cycles for high temperature CO_2 sequestration.
- Adsorption properties of the EPA developed HTlcs will be provided to USC for inclusion in their PSA models.

Acknowledgments

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